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ORGANIC SILICATE POLYMER AND LOW DIELECTRIC INSULATING LAYER
WHICH CONTAINS THE POLYMER
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Organic Silicate Polymer and Low Dielectric Insulating Layer
Which Contains the Polymer

ABSTRACT

The present invention is about low dielectric organic silicate polymer which possesses thermal stability and at the same time a good quality in membrane-forming, and excellent mechanical and dielectric characteristics. This invention provides the organic silicate polymer, a hydrolysis condensate of a) organic silane oligomers, which are defined by more than one kind of chemical formula, each of which takes the following form of chemical formula #1, and b) silane compounds, which are defined by more than one kind of chemical formula, each of which takes the following form of chemical formula #2; and the method of its production; compositions for forming insulating layers for semiconductor devices that use this method; the insulating layers to which they are applied; and the method of their production.

[Chemical formula #1]

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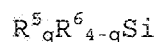


In the above chemical formula #1, R^1 is hydrogen, aryl, vinyl, allyl or alkyl which was not substituted or substituted with fluorine, with straight or branched chains, having one to four carbon atoms, R^2

*Numbers in the margin indicate pagination in the foreign text.

is $(CH_2)_aSR^3_pR^4_{3-p}$, n and m are the integers of zero (0) to ten (10) respectively. R^3 in the above R^2 is hydrogen, aryl, vinyl, allyl or alkyl which was not substituted or substituted with fluorine, with straight or branched chains, having one to four carbon atoms, R^4 is chlorine, acetoxy, hydroxyl or alkoxy, which was not substituted or substituted with fluorine, with straight or branched chains, having one (1) to four (4) carbon atoms. Here, p is an integer of zero (0) to two (2) and a is an integer of one (1) to six (6).

[Chemical formula #2]



In the above chemical formula #2, R^5 is hydrogen, aryl, vinyl, allyl or alkyl which was not substituted or substituted with fluorine, with straight or branched chains, having one (1) to four (4) carbon atoms, R^6 is chlorine, acetoxy, hydroxyl or alkoxy, with straight or branched chains, having one (1) to four (4) carbon atoms, and q is an integer of zero (0) to three (3).

When the organic silicate polymer of this invention is applied to insulating layers, the obtained layers have an excellent quality of insulating characteristics, equal distribution of coating and outstanding mechanical property of the coating.

[Glossary]

organic silicate polymer, organic silane oligomer, silane compounds, hydrolysis, condensates, low dielectric, semiconductor devices, insulating layers

Specification

Detailed description of the invention

The purpose of the invention

Technology to which the invention belongs and
The existing technology of the field

The present invention is about organic silicate polymer. The low dielectric organic silicate polymer possesses thermal stability and at the same time a good quality in membrane-forming, and excellent mechanical and dielectric characteristics. This invention provides the method of producing composites to form insulating layers for semiconductor devices that use this method, the insulating layers to which they are applied, and the method of their production.

Recently, as the degree of integration in semiconductor devices increases, the width of lines which connect the inside of the device is rapidly decreasing. It is expected that by the year 2003, highly condensed devices, using a circuit line width of 0.1 μm may be developed. Generally, the speed of the semiconductor device is proportionate to the switching speed of the transistor and transmitting speed of signals, and the transmitting speed of signals is determined by Resistive Capacitive delay, or RC delay, which is described as the multiplication of resistance of interconnecting material and capacitance of insulating films between the layers. As the degree of integration in semiconductor devices increases, the width between the interconnecting metallic wires of the devices

becomes narrow, and the thickness becomes thinner, and at the same time the length increases in geometrical progression. Thus, the high density on-chip speed is determined by its RC delay, rather than switching speed. For this reason, in order to produce high speed chips, low resistance conductor and insulating materials having low dielectricity should be used. Furthermore, using low dielectric materials not only increases the speed of the semiconductor devices, but also decreases electricity consumption. This can also /3 drastically reduce the cross-talk phenomenon between the interconnecting metallic wires, all of which are the advantages of using low dielectric materials.

Recently, IBM has marketed semiconductor testing products, which have improved more than 30% in capacity by using copper wires, which have high electrical conductivity, rather than using the conventional aluminum wires. On the other hand, semiconductor devices to which low dielectric materials are applied have not been marketed yet, due to the underdevelopment of appropriate materials.

The insulating material between layers of conventional semiconductor devices such as IC, LSI, etc. is mostly SiO_2 , whose dielectric constant is 4.0. As a low dielectric material, silicate (F-SiO_2) doped with fluorine is partially applied to some devices, but in the case of F-SiO_2 , there is a problem: when the percentage(%) of fluorine contained is more than 6%, it becomes thermally unstable. With this method, it is difficult to reduce the dielectric constant

below 3.5. Recently, in order to resolve this problem, various organic and inorganic macromolecules which are low in polarity and thermally stable have been introduced.

As organic macromolecules which possess a low dielectric constant, the following items are known: polyimide resin with or without fluorine, polyallylene ether resin and resin that contains perfluorocyclobutane, etc. The dielectric constant of these organic macromolecules is mostly 3.0. However, their problems are the elastic modulus in high temperature drastically drops, because the glass transition temperature is generally low and the coefficient of linear thermal expansion (CLTE) is very high. In addition, in the case of organic macromolecules, which contains fluorine, the quality of such material property further deteriorates. During the manufacturing and packaging process of semiconductors, the temperature may go up between 200 °C to 450 °C. Therefore, organic macromolecules that have such low thermal stability and elastic modulus and a high coefficient of linear thermal expansion may reduce dependability of the devices or wiring board.

In order to solve the problem of thermal stability of organic macromolecules as explained above, recently, the development of organic silicate macromolecules using a sol-gel process is in progress. This is a method of forming an organic silicate membrane through a curing process after hydrolysis and condensation reaction of organic silane. The hydrogen or methyl silsesquioxane which is

produced by this method has a low dielectric constant of 3.0 or less and thermal stability at 450 °C. However, there are problems with the above organic silicate macromolecules such as the occurrence of cracks at a thickness of 1 μm or more due to a high shrinkage stress which occurs during the curing process, and its mechanical strength is reduced drastically, due to the introduction of hydrogen or alkyl radical.

TECHNOLOGICAL TASK WHICH THIS INVENTION INTENDS TO ACHIEVE

In consideration of the above existing technical problems, the purpose of this invention is to provide a low dielectric material, which can be used as an extremely low dielectric insulating membrane between the wired layers. This enables the high speed of semiconductor devices, a decrease in electric consumption, and a drastic reduction in the cross-talk phenomenon between the interconnecting metallic wires.

Another purpose of this invention is to provide silica-based polymer, which has good membrane-forming characteristics, and excellent mechanical and dielectric properties and the method of their production, and to provide the insulating layers which contain the polymer and the method of their production.

COMPOSITION AND FUNCTION OF THE INVENTION

In order to achieve the above purposes, this invention provides

a) organic silane oligomers, which are defined by more than one kind of chemical formula, each of which takes the following form of

chemical formula #1; and b) an organic silicate polymer that is a hydrolysis condensate of silane compounds which are defined by more than one kind of chemical formula, each of which takes the following form of chemical formula #2:

[Chemical formula #1]

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In the above chemical formula #1,

R^1 is hydrogen, aryl, vinyl, allyl or alkyl which was not substituted or substituted with fluorine, with straight or branched chains, having one to four carbon atoms,

R^2 is $(\text{CH}_2)_a \text{SR}_p^3 \text{R}_{3-p}^4$,

n and m are integers of zero (0) to ten (10) respectively.

R^3 in the above R^2 is hydrogen, aryl, vinyl, allyl or alkyl which was not substituted or substituted with fluorine, with straight or branched chains, having one to four carbon atoms,

R^4 is chlorine, acetoxy, hydroxyl or alkoxy, which was not substituted or substituted with fluorine, with straight or branched chains, having one (1) to four (4) carbon atoms.

Here, p is an integer of zero (0) to two (2) and a is an integer of one (1) to six (6).

[Chemical formula #2]



In the above chemical formula #2,

R^5 is hydrogen, aryl, vinyl, allyl or alkyl which was not substituted or substituted with fluorine, with straight or branched chains, having one (1) to four (4) carbon atoms,

R^6 is chlorine, acetoxy, hydroxyl or alkoxy, with straight or branched chains, having one (1) to four (4) carbon atoms, and

q is an integer of zero (0) to three (3).

Also, in the method of producing the organic silicate polymer, this invention includes the following steps:

Step a) In an organic solvent, mixing

- i) organic silane oligomers, which are defined by more than one kind of chemical formula, each of which takes the above form of chemical formula #1; and
- ii) silane compounds which are defined by more than one kind of chemical formula, each of which takes the above form of chemical formula #2.

Step b) In the above compound, adding catalyst and water, and implementing the hydrolysis and condensation reaction. In this way, /5
the invention provides the method of producing the organic silicate polymer.

Also, in the composition of forming insulating membrane for semiconductor devices, this invention provides:

- a) i) organic silane oligomers, which are defined by more than one kind of chemical formula, each of which takes the above form of chemical formula #1; and ii) the organic silicate polymer that is a

hydrolysis condensate of silane compounds which are defined by more than one kind of chemical formula, each of which takes the above form of chemical formula #2; and

b) the composition of forming insulating membrane, including an organic solvent.

The above composition of forming insulating membrane

c) may include one or more selected additives from the group which consists of organic molecules such as organic polymer, organic dendrimer, colloidal silica, aerosol, georosol/ziorosol [as transliterated], and surfactant, according to the purpose.

Also, in the method of production of insulating membranes of semiconductor devices, this invention provides the following steps:

a) Providing composite solution for forming insulating membranes; i) a) organic silane oligomers, which are defined by more than one kind of chemical formula, each of which takes the following form of chemical formula #1; and
b) an organic silicate polymer that is a hydrolysis condensate of silane compounds, which are defined by more than one kind of chemical formula, each of which takes the following form of chemical formula #2; and ii) organic solvents.

b) forming the insulating membranes by coating the solution in the above step a) on the materials of the semiconductor devices.

c) drying and calcination of the insulating membranes formed in the above step b) and

d) treating the surface of the above insulating membranes when necessary.

The details of this invention are explained hereafter.

The present invention is about an organic silicate polymer, a hydrolysis condensate which is made by mixing a certain ratio between organic silane oligomers which are defined by chemical formula #1, and silane compounds, which are defined by chemical formula #2; and the method of their production; the composition, which contains this, for forming insulating layers; copolymerized organic silicate macromolecules insulating films between layers, which is made of these composites; and their production method.

When the organic silicate polymer of this invention is applied to insulating layers, outstanding mechanical properties, equal distribution of coating and excellent dielectric characteristics are obtained.

Regarding the composition ratio of the ingredients of the organic silicate polymer of this invention, there is no significant limitation between the two components of chemical formula #1 and #2. However, it is desirable to use organic silane oligomer of chemical formula #1 from 5 to 90 wt% of the entire composite, and more desirable in the range of 5 to 60 wt%.

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In manufacturing the above organic silicate polymer, of the compound defined as the above chemical formula #2, in the event that a compound with the value of q being 2 or 3 is used, it is desirable

to include less than 70 wt% of the total silane compound, and more desirable to include less than 40 wt%. In the event that more than this amount is used, it may cause a decrease in the mechanical strength of the membranes.

Water and catalysts are added to the mixture containing the compounds of the above chemical formulas #1 and #2, in the presence of the solvent, and hydrolysis and condensation reaction is conducted. Then an organic silicate macromolecule with a certain molecular weight is obtained. From this, a composite for forming insulating membrane is produced. There is no particular limitation in the order of mixing the compounds of the above chemical formulas #1 and #2. After the total amount that is to be used may be all mixed from the beginning, then hydrolysis condensation reaction may be carried out, or of the total amount to be used, hydrolysis condensation reaction of the fixed amount of the compounds of the chemical formulas #1 and #2 may be executed first in order to obtain a desired molecular weight, and then the rest may be added for further reactions.

The solvents which were used for the composition for polymerization or to form insulating layers in this invention are, for example aliphatic hydrocarbon solvents such as n-pentane, i-pentane, n-hexane, i-hexane, 2,2,4-trimethylpentane, cyclohexane, methylcyclohexane, etc.; aromatic hydrocarbon family such as benzene, toluene, xylene, trimethylbenzene, ethylbenzene, methylethylbenzene, etc.; alcohol family such as methyl alcohol, ethyl alcohol,

n-propanol, i-propanol, n-butanol, i-butanol, sec-butanol, t-butanol, cyclohexanol, methylcyclohexanol, glycerol, etc.; ether family such as tetrahydrofuran, 2-methyltetrahydrofuran, ethyl ether, n-propyl ether, isopropyl ether, diglime, dioxin, dimethyldioxin, ethyleneglycolmonomethyl ether, ethyleneglycoldimethyl ether, ethyleneglycoldiethyl ether, propyleneglycolmonomethyl ether, propyleneglycoldimethyl ether, etc.; ester family, such as diethylcarbonate, methyl acetate, ethyl acetate, ethylactate, ethylactate, ethyleneglycolmonomethyl ether acetate, propyleneglycolmonomethyl ether acetate, ethyleneglycoldiacetate, etc.; and amide family such as N-methylpyrrolidone, formamide, N-methylformamide, N-ethylformamide, N, N-dimethylacetamide, N, N-diethylacetamide, etc.

The solvents that were used in the hydrolysis and condensation reactions were all removed after the reaction to obtain organic silicate macromolecule oil or powder, and again, this organic silicate macromolecule may be dissolved in the organic solvent for membrane formation and used, or of the organic solvent which was used for the hydrolysis and condensation reaction, a fixed amount of a particular solvent which would negatively influence the coating quality needs to be removed. Thereafter, the organic solvent may be used directly for the membrane formation. It is possible to use a mixture of more than one or two kinds of the above solvents.

In this invention, in order to facilitate the hydrolysis

condensation reaction, it is desirable to use a catalyst. The catalyst that is used in this hydrolysis condensation reaction can be an acid catalyst, a base catalyst, a metal chelate compound, etc. For example as for an acid catalyst, hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid, formic acid, benzylsulfonic acid, toluenesulfonic acid, acetic acid, oxalic acid, malonic acid, maleinic acid, fumaric acid, citric acid, propionic acid, benzylsulfonic acid, toluenesulfonic acid, acetic acid, oxalic acid, malonic acid, maleinic acid, fumaric acid, citric acid, propionic acid, etc., are possible; as for a base catalyst, ammonia, calcium hydroxide, potassium hydroxide, trimethylamine, triethylamine, diethanolamine, triethanolamine, dimethyl ethyl alcohol amine, monomethyl diethanolamine diazabicycloundecene, pyridine, pyrrol piperidine; choline, pyrrolidine, piperazine, etc. are possible; as for a metal chelate compound, organic metallic compounds which are composed of metal, such as aluminum, titan, zirconium, tin, tantalum, platinum, etc., are possible. The above acid, base and metal chelate compounds may be used alone, or in combination. Also it is possible to use more than two kinds stepwise.

The added amount of such catalysts is between 0.0001 and 1 mole per 1 mole of a total silane compound used. However, it is more desirable to use less than 0.5 mole. In the event that the amount of catalyst is more than 1 mole per 1 mole of a silane compound, it is difficult to adjust the molecular weight, due to the very fast

reaction speed, and there is a possibility that a gel may easily occur.

In this invention, water is added for the hydrolysis of a silane compound. The appropriate amount of water for the hydrolysis of a silane compound is between 0.1 and 20 moles per 1 mole of silicon atom of the total silane compound used. The desired amount is between 1 and 10 moles. The method of adding water can be intermittent or continuous. At this time, the catalysts may be added to the organic solvent in advance or when water is added, it may dissolve or disperse. The reaction temperature at this time is between 0 °C and 100 °C. However, it is more desired to have the reaction between 15 °C and 80 °C. Average molecular weight of the obtained hydrolysis condensate is between 500 and 1,000,000. The desirable range is between 1000 and 1,000,000. /7

In the obtained composite for membrane formation in this invention, a certain amount of organic molecules such as organic polymers and dendrimer may well be added in order to further reduce the density. There is no significant restriction in the kinds of organic compounds. However, organic molecules or macromolecules composed of materials which enable pyrolysis at the temperatures between 200 °C and 450 °C, for example, aliphatic hydrocarbon, aromatic hydrocarbon, ether functional group, ester functional group, anhydride functional group, carbonate functional group, acryl functional group, thioether functional group, isocyanate functional

group, isocyanurate functional group, sulfonate functional group, and sulfoxide functional group, etc. may be used. The above organic molecules or organic macromolecules may contain alkoxysilane functional group, at the end of or inside the molecules, which can react with organic silicate. Regarding the use of the above organic polymer and dendrimer, they may be added to the composite for membrane formation or they may also be added at the time of producing the organic silicate polymer.

In the obtained composite for membrane formation in this invention, a certain amount of other ingredients such as colloidal state silica, aerosol, georosol/ziorosol [as transliterated], surfactant, etc. may be added according to the purpose.

The total solid content of the composite of this invention is between 2 and 60 wt%. Considering the thickness of the insulating membrane and its preservation and safety, the desirable range is between 5 and 40 wt%. The total solid content here is adjustable based on the amount of the above organic solvents used.

The composite for insulating membrane formation in this invention forms insulating layers by coating materials such as silicon wafer, SiO_2 wafer, SiN wafer, compound semiconductor, etc. As for the method of forming the insulating layers, a spin coat method, precipitation method, roll-coating method, spray method, etc. may be used. By using these methods, it is possible to form a certain thickness of the membrane. Among them, for the purpose of producing

the insulating membranes, between layers in the multilayer circuit board, the spin coat method is appropriate.

The thickness of the membrane is adjustable by changing the viscosity of the composites and the revolving speed of the spin coater. Generally, for the purpose of using as structure of the semiconductor device the appropriate thickness is between 0.5 and 2 μm .

After coating is done, the organic silicate macromolecule insulating membrane of 3-dimensional structure can be formed through drying process and calcination (curing) process. Usually drying temperature and calcination temperature are between 30 ° C and 300 °C and between 300 °C and 600 °C, respectively. Especially, the desirable calcination temperatures are between 350 °C and 500 °C. In the event that the calcination temperature becomes higher than 600 °C, the thermal stability of organic silicate macromolecules drops, and on the other hand, when the temperature drops less than 300 °C, the condensation of the organic silicate macromolecule is incomplete. Thus, the strength of the membrane becomes weak, and there is a possibility that the dielectric characteristics may be reduced due to the presence of the remaining functional groups.

The drying process and calcination process may be performed continually, heating with a predetermined speed. Also they may be done intermittently. In the event that they are performed intermittently, it is appropriate to be done from 1 minute to 5 hours

respectively. As for the method of heating, a hot plate, an oven, a furnace, etc. may be used. Regarding the heating atmosphere, it is possible to perform under an inert gas atmosphere such as nitrogen, argon, helium, etc.; oxygen atmosphere like oxygen containing gas atmosphere for example the air, etc.); or gas atmosphere that contains vacuum state or ammonia and hydrogen. Regarding the above heating method, both the drying process and calcination process may use the same heating method, or both processes may use a different method.

After finishing the drying process and calcination process, /8
the surface treatment was carried out as needed in order to minimize the amount of hydroxy group inside the insulating membrane. Regarding the method of surface treatment, the generally known silyl compounds such as Hexamethyldisilazane, alkylchlorosilane, alkylalkoxy silane, alkylacetaloxy silane may be used. The surface treatment may also be possible under reducing atmosphere like hydrogen or by calcination under fullerene containing gas. The silylation treatment method of insulating membranes may be possible by dipping or spin coating in the silylation compound or a silylation compound which is diluted in a solvent, or it can be carried out under the steam atmosphere of the silylation compound. After the silylation treatment, it is desirable to heat the insulating membrane between 100 °C and 400 °C.

The membrane obtained through such processes retains insulating properties, equal distribution of coating, dielectric characteristics,

crack resistance, surface strength, all of which are excellent. Therefore, the membrane may be well suitable to be used as an insulating membrane between layers of semiconductor devices such as LSI, System LSI, DRAM, SDRAM, RDRAM, D-RDRAM, etc., protective coating such as surface coating of semiconductor devices the insulating membrane between layers of the multilayer wiring boards, protective coating, or insulating membranes for liquid crystal display (LCD) devices, etc.

This invention is explained further in detail through the following practical examples and comparisons. However, the intention of the practical examples is to illustrate the invention. They are not limited by themselves alone:

[PRACTICAL EXAMPLES]

Example 1.

(Production of Organic Silicate Condensate)

After 12.5g of vinyltrimethoxy silane and 50 μ l of platinum catalyst were put into a completely dried reaction container, they were first reacted for 15 minutes at room temperature. Thereafter, 5.0 ml of tetramethylcyclo silane was added and allowed to react under the 50 °C nitrogen atmosphere for 10 hours. After the remaining reactants were completely removed under vacuum, it was confirmed through the NMR spectrum that the reaction progressed completely.

After 2.67 ml of the above product, 13.8 ml of methyltrimethoxy silane, and 30 ml of tetrahydrofuran were put into a different

container, 5.9 ml of water, and 1.0 ml of hydrochloric acid of 5.0 M concentration were slowly added with agitation under a nitrogen atmosphere. After letting them react for 30 minutes at room temperature, the temperature was gradually increased up to 60 °C and the heat-reflux was made. Then, the reaction took place overnight.

After the completion of the reactions, a dilution was made with ether solvent and the washing with water was done until the pH reached neutral. The obtained solvent of the organic phase was completely removed in the vacuum oven and a powder form of product was obtained.

(Manufacturing Insulating Membranes)

The above obtained powder 300mg was dissolved in methyl isobutyl cation to make the total solution of 1.5g. After the impurities in the obtained solution were removed through filters, thin layers were obtained through spin coating. The insulating membranes were produced through the drying and calcination processes under nitrogen atmosphere.

Example 2.

(Production of Organic Silicate Condensate)

After 14.6g of allyltrimethoxysilane and 50 μ l of platinum catalyst were put into a completely dried reaction container, they were first reacted for 15 minutes at room temperature. Thereafter, 5.0 ml of tetramethylcyclo silane was added and allowed to react under the 50 °C nitrogen atmosphere for 10 hours. After the remaining

reactants were completely removed under vacuum, it was confirmed by the NMR spectrum that the reaction progressed completely.

After 2.67 ml of the above product, 2.5 ml of tetramethoxysilane, 11 ml of methyltrimethoxy silane, and 30 ml of tetrahydrofuran were put into a different container, 5.9 ml of water, and 1.0 ml of hydrochloric acid of 5.0 M concentration were slowly added with agitation under nitrogen atmosphere. After letting them react for 30 minutes at room temperature, the temperature was gradually increased up to 60 °C and the heat-reflux was made. Then, the reaction took place overnight.

After the completion of the reactions, a dilution was made with ether solvent and the washing with water was done until the pH reached neutral. The obtained solvent of the organic phase was completely removed in the vacuum oven and a powder form of product was obtained.

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(Manufacturing Insulating Membranes)

The insulating membranes were produced from the above obtained powder, through the drying and calcination processes with the same way as presented in example 1.

Comparison 1.

After mixing 7.5 ml of methyltrimethoxy silane and 4.05 ml of distilled water in 15 ml of tetrahydrofuran solvent, 0.80 ml of hydrochloric acid with 2N concentration was gradually added with agitation under nitrogen atmosphere.

After letting them react for 30 minutes at room temperature, the temperature was gradually increased up to 60 °C and the heat-reflux was made. Then, the reaction took place overnight.

After the completion of the reactions, a dilution was made with ether solvent and the washing with water was done until the pH reached neutral. The obtained solvent of the organic phase was completely removed in the vacuum oven and a powder form of product was obtained.

(Manufacturing Insulating Membranes)

The insulating membranes were produced from the above obtained powder, through the drying and calcination processes with the same way as presented in Example 1.

(Measurement of the Properties)

Regarding the molecular weight (the weight average molecular weight: Mw) of organic silicate macromolecule, which was produced in the above Practical Examples 1 and 2, and Comparison 1, the value of the relative molecular weight was obtained through Gel Permeation Chromatography (GPC) with polystyrene as a standard.

Also, the mechanical properties of each individual thin layer were measured, after spin coating was done on a 2x2 inch Si wafer, and then hardening was done under N₂ condition at 430 °C for one (1) hour.

In addition, the dielectric characteristics of each individual coating was measured, after making MIM (Metal Insulator

Semiconductor) device on the Si wafer, using the HP company's LCR meter at 1 Mhz.

Furthermore, regarding the crack resistance of each thin layer, thin layers with their thickness of 1 μm were produced and then whether the cracks occur was observed.

The results of the above experiments are presented in the following table 1.

[Table 1]

Category	Example 1	Example 2	Comparison 1
Molecular Weight (Mw)	22000	8860	10100
Dielectric Constant	2.51	2.56	2.68
Crack Velocity	2.8e^{-12}	3.4e^{-12}	8.3e^{-9}

As understandable from the above Table 1, when thin layers are made with organic silicate macromolecules which are manufactured from this invention, the dielectric characteristics are excellent and the crack resistance is improved.

THE IMPACT OF THE INVENTION

The organic silicate polymer of this invention

When the organic silicate polymer of this invention is applied to insulating layers, the insulating properties, equal distribution of coating, dielectric characteristics, and mechanical characteristics are all excellent.

Claim 1.

In the organic silicate polymer, the organic silicate polymer, which is a hydrolysis condensate of

a) organic silane oligomers, which are defined by more than one kind of chemical formula, each of which takes the following form of chemical formula #1; and

b) silane compounds, which are defined by more than one kind of chemical formula, each of which takes the following form of chemical formula #2:

[Chemical formula #1]



In the above chemical formula #1,

R^1 is hydrogen, aryl, vinyl, allyl or alkyl which was not substituted or substituted with fluorine, with straight or branched chains, having one to four carbon atoms,

R^2 is $(\text{CH}_2)_a \text{SR}^3_p \text{R}^4_{3-p}$,

n and m are the integers of zero (0) to ten (10) respectively.

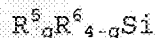
R^3 in the above R^2 is hydrogen, aryl, vinyl, allyl or alkyl which was not substituted or substituted with fluorine, with straight or branched chains, having one to four carbon atoms,

R^4 is chlorine, acetoxy, hydroxyl or alkoxy, which was not substituted or substituted with fluorine, with straight or branched

chains, having one (1) to four (4) carbon atoms.

Here, p is an integer of zero (0) to two (2) and a is an integer of one (1) to six (6).

[Chemical formula #2]



In the above chemical formula #2,

R^5 is hydrogen, aryl, vinyl, allyl or alkyl which was not substituted or substituted with fluorine, with straight or branched chains, having one (1) to four (4) carbon atoms,

R^6 is chlorine, acetoxy, hydroxyl or alkoxy, with straight or branched chains, having one (1) to four (4) carbon atoms, and

q is an integer of zero (0) to three (3).

Claim 2.

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In Claim 1,

the organic silicate polymer, which contains organic silane oligomer from 5 to 90 wt% in the above chemical formula #1.

Claim 3.

In Claim 1,

the organic silicate polymer, whose weight average molecular weight is between 500 and 1,000,000.

Claim 4.

In the method of manufacturing the organic silicate polymer, this invention includes the following steps:

Step a) In an organic solvent, mixing

i) organic silane oligomers, which are defined by more than one kind of chemical formula, each of which takes the above form of chemical formula #1; and

ii) silane compounds which are defined by more than one kind of chemical formula, each of which takes the above form of chemical formula #2:

Step b) In the above compound, adding catalyst and water and implementing the hydrolysis and condensation reaction:

[Chemical formula #1]



In the above chemical formula #1,

R^1 is hydrogen, aryl, vinyl, allyl or alkyl which was not substituted or substituted with fluorine, with straight or branched chains, having one to four carbon atoms,

R^2 is $(\text{CH}_2)_a \text{SR}^3_p \text{R}^4_{3-p}$.

n and m are the integers of zero (0) to ten (10) respectively.

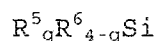
R^3 in the above R^2 is hydrogen, aryl, vinyl, allyl or alkyl which was not substituted or substituted with fluorine, with straight or branched chains, having one to four carbon atoms,

R^4 is chlorine, acetoxy, hydroxyl or alkoxy, which was not substituted or substituted with fluorine, with straight or branched chains, having one (1) to four (4) carbon atoms.

Here, p is an integer of zero (0) to two (2) and a is an integer of one (1) to six (6).

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[Chemical formula #2]



In the above chemical formula #2,

R^5 is hydrogen, aryl, vinyl, allyl or alkyl which was not substituted or substituted with fluorine, with straight or branched chains, having one (1) to four (4) carbon atoms,

R^6 is chlorine, acetoxy, hydroxyl or alkoxy, with straight or branched chains, having one (1) to four (4) carbon atoms, and

q is an integer of zero (0) to three (3).

Claim 5.

In Claim 4, the method of manufacturing the polymer,

the compound in the above step a) is the organic silicate polymer, which contains organic silane oligomer from 5 to 90 wt% in the above chemical formula #1.

Claim 6.

In Claim 4, the method of manufacturing the polymer,

in the above step b), the added amount of the catalyst is between 0.0001 and 1 mole per 1 mole of a total silane compound condensed.

Claim 7.

In Claim 4, the method of manufacturing the polymer,

in the above step b), the amount of water added is between 0.1 and 20 moles per 1 mole of silicon atom of the total silane compound condensated.

Claim 8.

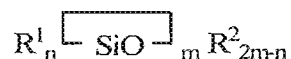
In the composition of forming insulating membrane for semiconductor devices, the composition includes:

a) i) organic silane oligomers, which are defined by more than one kind of chemical formula, each of which takes the following form of chemical formula #1; and ii) the organic silicate polymer that is a hydrolysis condensate of silane compounds which are defined by more than one kind of chemical formula, each of which takes the following form of chemical formula #2; and

b) organic solvent:

[Chemical formula #1]

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In the above chemical formula #1,

R^1 is hydrogen, aryl, vinyl, allyl or alkyl which was not substituted or substituted with fluorine, with straight or branched chains, having one to four carbon atoms,

R^2 is $(\text{CH}_2)_a \text{SR}^3_p \text{R}^4_{3-p}$,

n and m are the integers of zero (0) to ten (10) respectively.

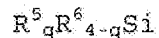
R^3 in the above R^2 is hydrogen, aryl, vinyl, allyl or alkyl which was not substituted or substituted with fluorine, with straight or

branched chains, having one to four carbon atoms,

R^4 is chlorine, acetoxy, hydroxyl or alkoxy, which was not substituted or substituted with fluorine, with straight or branched chains, having one (1) to four (4) carbon atoms.

Here, p is an integer of zero (0) to two (2) and a is an integer of one (1) to six (6).

[Chemical formula #2]



In the above chemical formula #2,

R^5 is hydrogen, aryl, vinyl, allyl or alkyl which was not substituted or substituted with fluorine, with straight or branched chains, having one (1) to four (4) carbon atoms,

R^6 is chlorine, acetoxy, hydroxyl or alkoxy, with straight or branched chains, having one (1) to four (4) carbon atoms, and

q is an integer of zero (0) to three (3).

Claim 9.

In Claim 8,

the above composition

c) includes one or more selected additives from the group which consists of organic molecules such as organic polymer, organic dendrimer, colloidal silica, aerosol, geosol/ziorosol [as transliterated], and surfactant in order to form insulating membrane for semiconductor devices.

Claim 10.

In Claim 8 or 9,

The above composition is for forming insulating membrane for /14 semiconductor devices. The total solid content of the composite is between 2 and 60 wt%.

Claim 11.

In the method of production of insulating membranes of semiconductor devices, this invention provides the following steps:

a) Providing the composite solution for forming insulating membranes: i) a) organic silane oligomers, which are defined by more than one kind of chemical formula, each of which takes the following form of chemical formula #1; and b) an organic silicate polymer that is a hydrolysis condensate of silane compounds, which are defined by more than one kind of chemical formula, each of which takes the following form of chemical formula #2; and ii) organic solvents.

b) forming the insulating membranes by coating the solution in the above step a), upon the materials of the semiconductor devices.

c) drying and calcination of the insulating membranes formed in the above step b).

[Chemical formula #1]



In the above chemical formula #1,

R^1 is hydrogen, aryl, vinyl, allyl or alkyl which was not

substituted or substituted with fluorine, with straight or branched chains, having one to four carbon atoms,

R^2 is $(CH_2)_aSR^3_pR^4_{3-p}$,

n and m are the integers of zero (0) to ten (10) respectively.

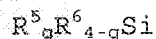
R^3 in the above R^2 is hydrogen, aryl, vinyl, allyl or alkyl which was not substituted or substituted with fluorine, with straight or branched chains, having one to four carbon atoms,

R^4 is chlorine, acetoxy, hydroxyl or alkoxy, which was not substituted or substituted with fluorine, with straight or branched chains, having one (1) to four (4) carbon atoms.

Here, p is an integer of zero (0) to two (2) and a is an integer of one (1) to six (6).

[Chemical formula #2]

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In the above chemical formula #2,

R^5 is hydrogen, aryl, vinyl, allyl or alkyl which was not substituted or substituted with fluorine, with straight or branched chains, having one (1) to four (4) carbon atoms,

R^6 is chlorine, acetoxy, hydroxyl or alkoxy, with straight or branched chains, having one (1) to four (4) carbon atoms, and

q is an integer of zero (0) to three (3).

Claim 12.

In Claim 11, the method of manufacturing insulating membranes, in the above step b) [sic. Translator's note: this should be

step c1, the drying temperature is between 30 °C and 300 °C and the calcination temperature is between 300 °C and 600 °C respectively.

Claim 13.

The insulating layers of semiconductor devices manufactured according to the method described in Claim 11.

Claim 14.

The semiconductor devices including the insulating layers manufactured according to the method described in Claim 11.